

The Nitration of 2,4,5-Trimethylphenol, 3,4,6-Trimethyl-2-nitrophenol and Their Acetates

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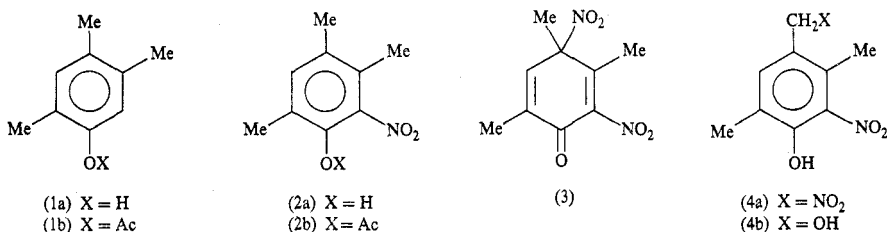
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Abstract

Nitration with fuming nitric acid of 2,4,5-trimethylphenol (1a), its acetate (1b), 3,4,6-trimethyl-2-nitrophenol (2a) or its acetate (2b) gives the 3,4,6-trimethyl-2,4-dinitrocyclohexa-2,5-dienone (3) in high yield. Some transformations of this dinitro ketone (3) are described.

Introduction

In the course of studies on the polynitration of phenols, we found it necessary to re-examine a reaction reported by Auwers in 1896.¹ He nitrated 2,4,5-trimethylphenol (1a) to give a crystalline compound, m.p. 81°, of molecular formula $C_9H_{10}N_2O_5$ and tentatively assigned to it the dinitro ketone structure (3). We can now report spectroscopic data which confirms this structure and we have clarified some reactions of the dinitro ketone (3).¹



Discussion

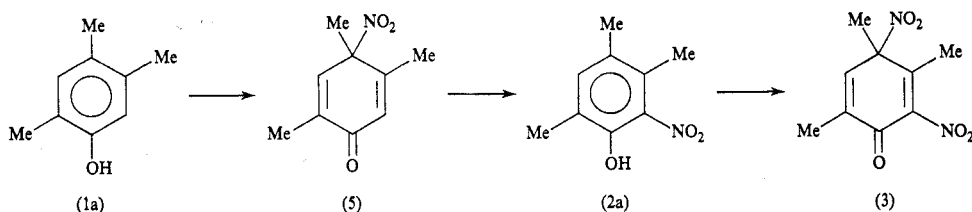
The dinitro ketone (3) was formed in high yield (about 90%) from 2,4,5-trimethylphenol (1a), from its acetate (1b), from 3,4,6-trimethyl-2-nitrophenol (2a), or from its acetate (2b), by brief reaction with neat fuming nitric acid at ice-salt temperatures. The infrared [1675 cm^{-1} (conjugated C=O), $1540\text{--}1570$ (NO₂) cm^{-1}] and ultraviolet [λ_{max} (CHCl₃) 250 nm, ϵ 7500] spectra were consistent with the assigned structure. In the ¹H n.m.r. spectrum of the dinitro ketone (3) the signal due to the vinylic proton at δ 6.73 appeared as a quartet and coupled to the adjacent C6 methyl group centred at 2.00, J 2 Hz. The remaining protons were accounted for by two methyl singlets at δ 2.00 and 2.05. The ¹³C n.m.r. spectrum, which revealed the presence of three methyl groups, a vinylic methine carbon, a quaternary carbon

¹ Auwers, K., *Ber. Dtsch. Chem. Ges.*, 1896, 29, 1095.

atom, three vinylic carbon atoms and a carbonyl carbon atom, was consistent with the assigned structure.

Treatment of the dinitro ketone (3) with ammonia in dry tetrahydrofuran, followed by acidification and extraction with ether, gave a crude product from which the dinitro phenol (4a) was isolated by chromatography. The structure of this compound (m.p. 110–111°, assumed to be the unidentified dinitro phenol isolated by Auwers¹) followed from its spectroscopic data. In particular, in its ¹H n.m.r. spectrum the signal due to C4–CH₂NO₂ at δ 5.67 appeared as a two-proton singlet, while the signals for the C3 and C6 methyls overlapped and appeared as a somewhat broadened six-proton singlet at δ 3.32.

Reaction of the dinitro ketone (3) with alcoholic ammonia solution gave a crude product which was shown (¹H n.m.r.) to consist mainly of the hydroxy nitro phenol (4b) (90%), but containing some dinitro phenol (4a). An analytical sample of the hydroxy nitro phenol (4b) was obtained by crystallization.



Scheme 1

The formation of the dinitro ketone (3) in high yield from each of the compounds (1a), (1b), (2a) and (2b) suggests that it is formed from 2,4,5-trimethylphenol (1a) by the reaction sequence in Scheme 1. For each phenyl acetate (1b) and (2b), nitronium ion attack *ipso* to the C4 methyl group, followed by acylium ion loss, would give rise to the corresponding 4-nitrocyclohexa-2,5-dienones (5) and (3).

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrometer as Nujol mulls; ¹H n.m.r. spectra on a Varian T60 or A60 spectrometer in CDCl₃ with SiMe₄ as an internal standard; ¹³C n.m.r. spectra on a Varian CFT20 for CD₃COCD₃ solutions with SiMe₄ as an internal standard. Ultraviolet spectra were run in chloroform solvent on a Shimadzu MPS-50L spectrometer. Silica gel for column chromatography was Crossfield's Sorbsil, grade B.S.S. The fuming nitric acid used was Analar grade, sp. gr. 1.5.

3,4,6-Trimethyl-2-nitrophenyl Acetate (2b)

3,4,6-Trimethyl-2-nitrophenol (2a) (2 g)¹ was added to acetyl chloride (5 ml) and the solution heated under reflux for 5 h. The crude product was isolated by means of ether and, on crystallization from light petroleum, gave the *acetate* (2b) (1.6 g), m.p. 82.5–83.5° (Found: C, 59.3; H, 5.9; N, 6.3. C₁₁H₁₃NO₄ requires C, 59.2; H, 5.9; N, 6.3%). $\nu_{\max}$ 1775, 1170 (OAc), 1530 (NO₂) cm⁻¹. ¹H n.m.r. δ 2.08, s, 6H, Me; 2.20, s, 6H, Me; 7.07, s, H5.

3,4,6-Trimethyl-2,4-dinitrocyclohexa-2,5-dienone (3)

(A) *From 2,4,5-trimethylphenol (1a).*—The phenol (5 g) was added slowly to stirred fuming nitric acid (30 ml) cooled in an ice-salt bath. The resulting red solution was added immediately to ice-water (400 ml), and the solid which separated was collected by filtration and washed thoroughly with cold water, cold ethanol and finally ether to afford the pure dinitro dienone (3) (4.35 g), m.p.

81–82° (Found: C, 48.0; H, 4.4; N, 11.9. Calc. for $C_9H_{10}N_2O_5$: C, 47.8; H, 4.5; N, 12.4%). It gave the following spectroscopic data. $\nu_{\max}$ 1675, 1540–1570 cm^{-1} . $\lambda_{\max}$ (CHCl₃) 250 nm (ϵ 7500). 1H n.m.r. δ 2.00, s, Me; 2.00, d, $J_{Me,H}$ 2 Hz, 6-Me; 2.05, s, Me; 6.73, q, $J_{H,Me}$ 2 Hz, H5. ^{13}C n.m.r. δ 14.38, 3-Me; 15.31, 6-Me; 22.62, 4-Me; 89.58, C4; 137.12, C3; 141.27, C5; 143.95, C6; 163.84, C2; 175.84, C1.

(B) From 2,4,5-trimethylphenyl acetate (1b), 3,4,6-trimethyl-2-nitrophenol (2a)¹ and 3,4,6-trimethyl-2-nitrophenyl acetate (2b).—The nitration of each substrate, as above, gave the dinitro dienone (3) (c. 90% yield).

Rearrangements of 3,4,6-Trimethyl-2,4-dinitrocyclohexa-2,5-dienone (3)

(A) With ammonia in tetrahydrofuran.—The dinitro dienone (3) (1 g) was dissolved in tetrahydrofuran (10 ml) saturated with ammonia and the solution kept at 20° for 30 min. The crude product (909 mg), isolated by acidification and extraction by means of ether, was shown (1H n.m.r.) to be largely (c. 90%) the dinitro phenol (4a). Pure dinitro phenol (4a) was isolated by chromatography on silica gel as needles (light petroleum), m.p. 110–111° (lit.¹ 110°). $\nu_{\max}$ 3200–3400 (OH), 1540 (NO₂) cm^{-1} . 1H n.m.r. δ 2.32, s, 6H, Me; 5.67, s, 2H, 4-CH₂NO₂; 7.33, s, H5; 10.20, s, OH (Found: C, 47.8; H, 4.5; N, 12.2. $C_9H_{10}N_2O_5$ requires C, 47.8; H, 4.5; N, 12.4%).

(B) With ammonia in ethanol.—The dinitro dienone (3) (500 mg) was dissolved in ethanol (5 ml), saturated with ammonia and the solution kept at 20° for 30 min. The crude product (297 mg), isolated by acidification and extraction by means of ether, was shown (1H n.m.r.) to consist largely (c. 90%) of hydroxy nitro phenol (4b), but containing some dinitro phenol (4a). Pure hydroxy nitro phenol (4b), obtained by crystallization from pentane, had m.p. 94–95°. $\nu_{\max}$ 3550, 3200–3300 (OH), 1533 (NO₂) cm^{-1} . 1H n.m.r. δ 2.29, s, Me; 2.35, s, OH; 2.40, s, Me; 4.67, s, 2H, 4-CH₂OH; 7.28, s, H5; 10.15, s, OH (Found: C, 54.8; H, 5.6; N, 7.2. $C_9H_{11}NO_4$ requires C, 54.8; H, 5.6; N, 7.1%).

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